Evaluation of a CO_2 Mitigation Option for California Coastal Power Plants: *Using Marine Chemistry to Mitigate CO_2 and Ocean Acidification*

Greg H. Rau
Institute of Marine Sciences, University of California, Santa Cruz, and
Carbon Management Program, Lawrence Livermore National Laboratory
rau4@llnl.gov

Thanks to CEC's EISG Program for funding

Ocean CO_2 Sequestration Options

- Physical: Deep ocean CO_2 injection (Marchetti, ‘77)
  issues - Cost of CO_2 capture and transport; Bio effects
- Biological: Ocean fertilization (Martin, ‘90)
  issues - Bio and eco effects; Mitigation effectiveness?
- Chemical:
  - Alkalinity addition (Kheshgi ‘95; House et al. ‘07; Harvey ‘08)
  - Enhanced limestone weathering (Rau et al. ‘99-’07)
- Other? E.g., crop waste stored in marine anoxic zones (Metzger and Benford, 2001)

Using Aqueous Chemistry to Capture/Store CO_2

Excess CO_2 readily reacts with:

1) water to form dissolved bicarbonate:

$CO_2 + H_2O$ <-----> H_2CO_3 <-----> $2H^+ + 2HCO_3^-$

2) water and dissolved carbonate to form dissolved bicarbonate:

$CO_2 + 2H_2O + CO_3^{2-}$ <---> $2H^+ + 2HCO_3^-$

3) water and carbonate minerals to form bicarbonate:

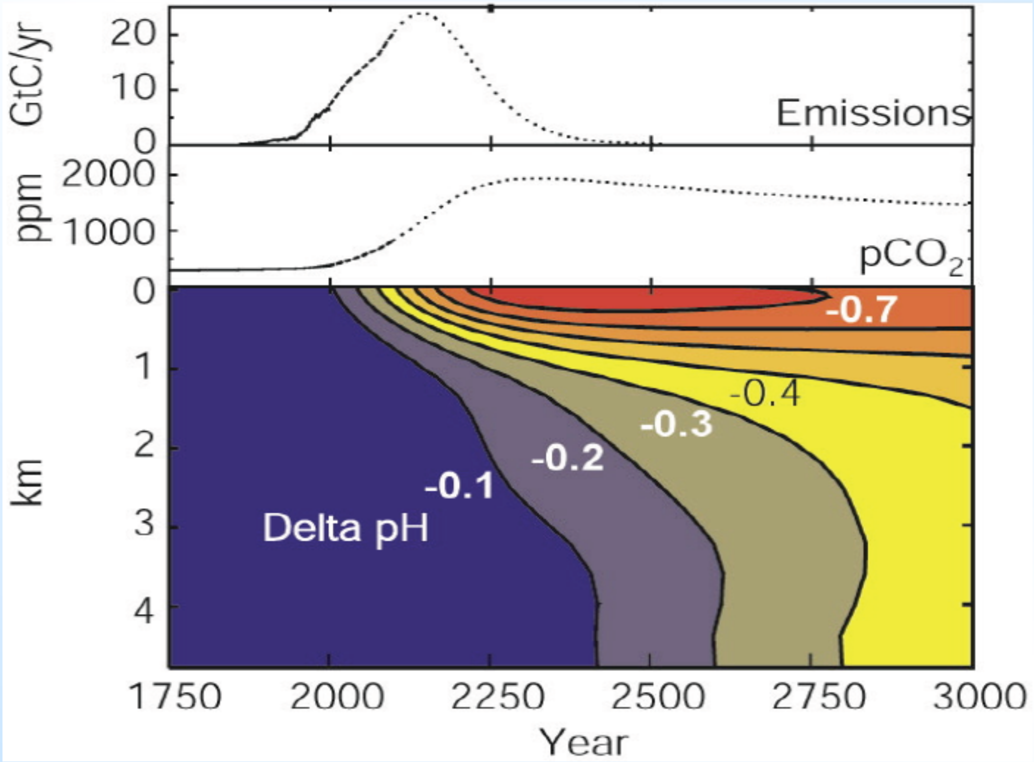
$CO_2 + H_2O + CaCO_{3(s)}$ <---> $Ca^{2+} + 2HCO_3^-$

With carbonate-rich water covering 70% of the planet, it is therefore not surprising that reactions 1-3 play the dominant role in modulating atmospheric CO_2. 1/3 to 1/2 of all anthropogenic CO_2 has thus far been consumed by reactions 1 and 2. However, there is a severe penalty for using reactions 1 and 2 for ocean CO_2 mitigation --->

Direct Ocean Absorption of CO_2 Causes Ocean Acidification

$CO_2 + H_2O$ <—> H_2CO_3 <—> $H^+ + HCO_3^-$ <—> $2\ H^+ + CO_3^{2-}$

(% of initial CO_2) : (+ 9 %) (+151 %) (– 60%)



(Caldeira and Wickett, 2003, *Nature* 425:365)

Therefore unlike climate effects, ocean acidification is guaranteed under BAU emissions scenarios

The consequences of increasing ocean acidity

- Significant impacts observed on calcifying organisms such as corals and shellfish
- Significant potential for impacts on marine ecosystems and biogeochemistry that are essential to a habitable planet, i.e. food and O_2 production, carbon and nitrogen cycling, etc.

O. Hoegh-Guldberg, et al., *Science*, December 2007

However, Reaction with Mineral Carbonates Reduces Ocean Acidification

Rather than:

$CO_2 + H_2O$ -----> H_2CO_3 -----> $2H^+$ + $2HCO_3^-$ (reactions 1 and 2)

Acid generation is avoided using carbonate minerals:

$CO_2 + H_2O + CaCO_{3(s)}$ ---> Ca^{2+} + $2HCO_3^-$ (reaction 3)
mimics natural CO_2 absorption via limestone weathering, hence the term accelerated weathering of limestone - AWL

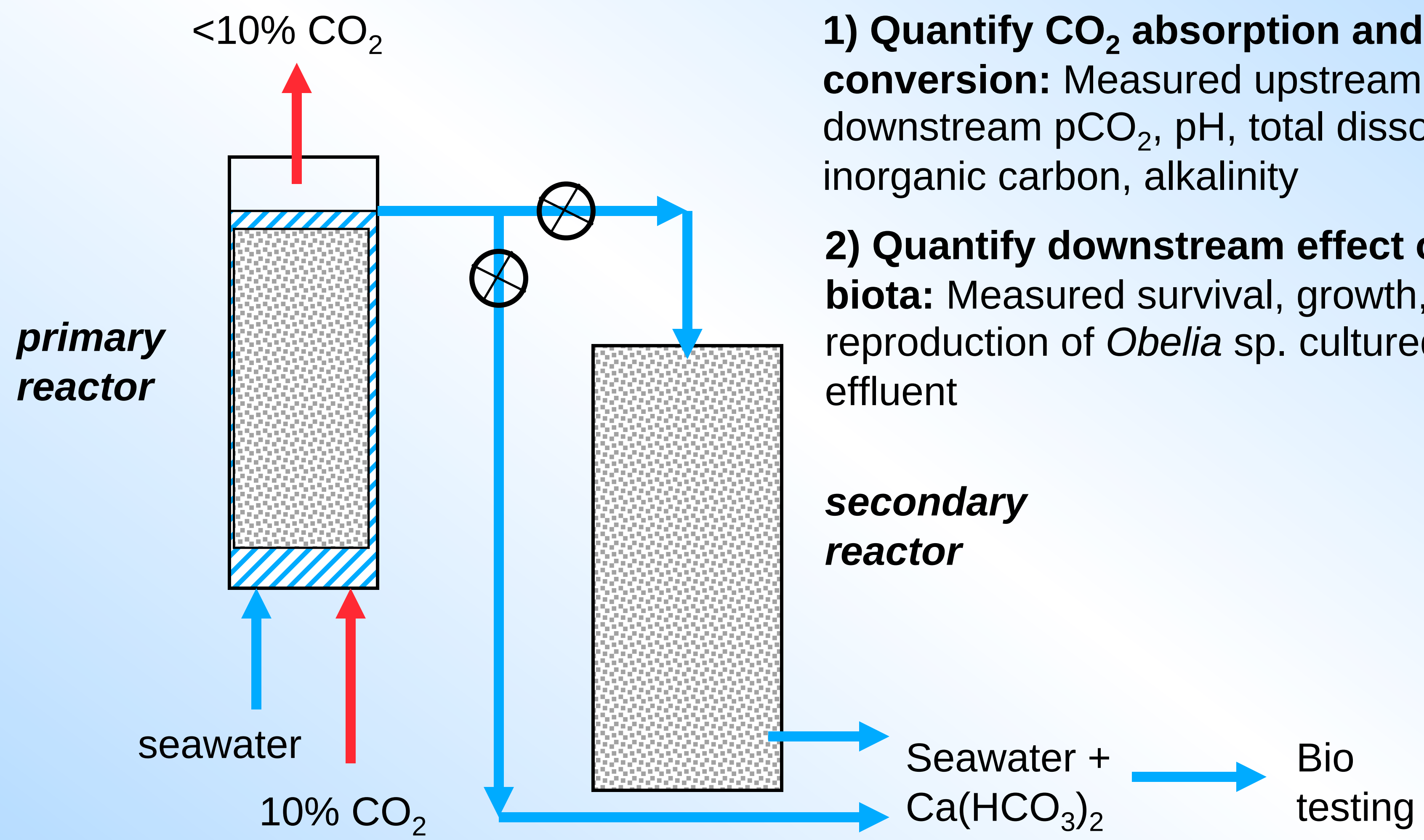
Therefore, because in many locations water (seawater) and carbonate minerals (limestone) are abundant and cheap, why not employ reaction 3 to mitigate point source CO_2 where cost effective to do so? Wet limestone scrubbing already used for SO_2 mitigation.

Proof of Concept: EISG/CEC funded project

Bench-scale evaluation of AWL concept at UCSC's Long Marine Laboratory

Adaptation of commercial seawater calcium/alkalinity generator to test effectiveness and safety of wet carbonate scrubbing of a 10% CO_2 stream:

Experimental Scheme:

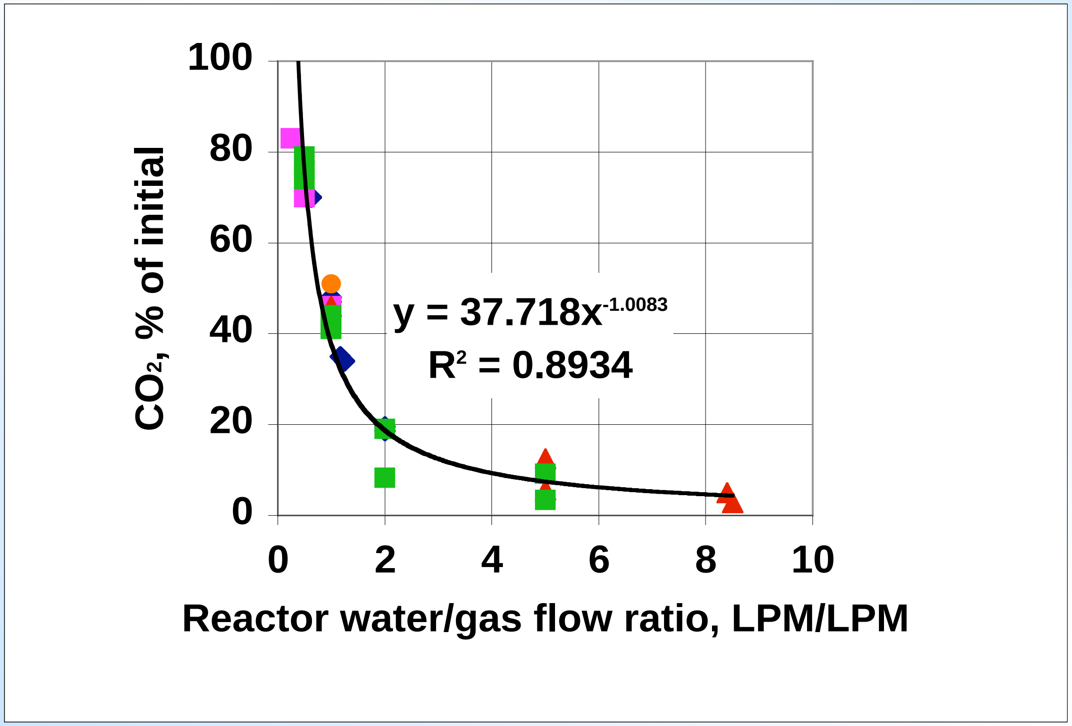


1) Quantify CO_2 absorption and conversion: Measured upstream and downstream pCO_2, pH, total dissolved inorganic carbon, alkalinity

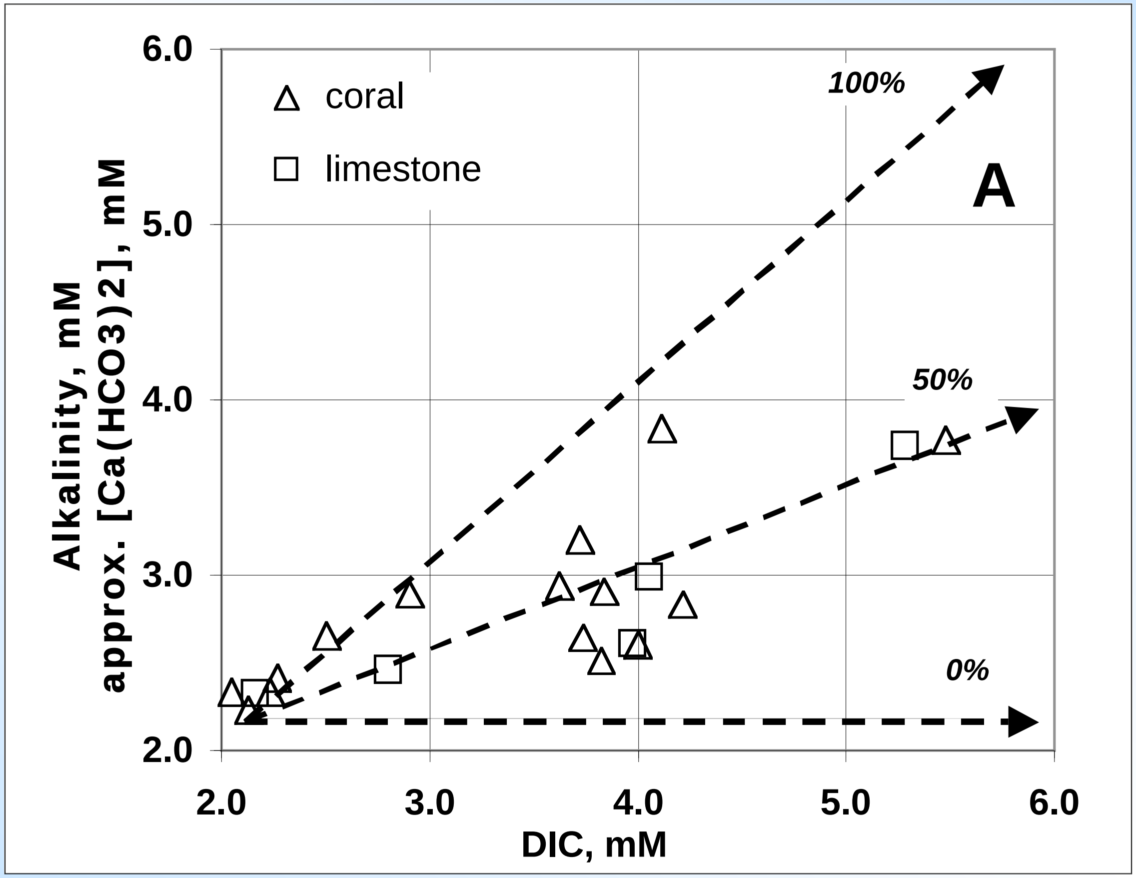
2) Quantify downstream effect on biota: Measured survival, growth, and reproduction of *Obelia* sp. cultured in effluent

Project results:

- Up to 97% removal CO_2 stream depending on water/gas flow ratio:

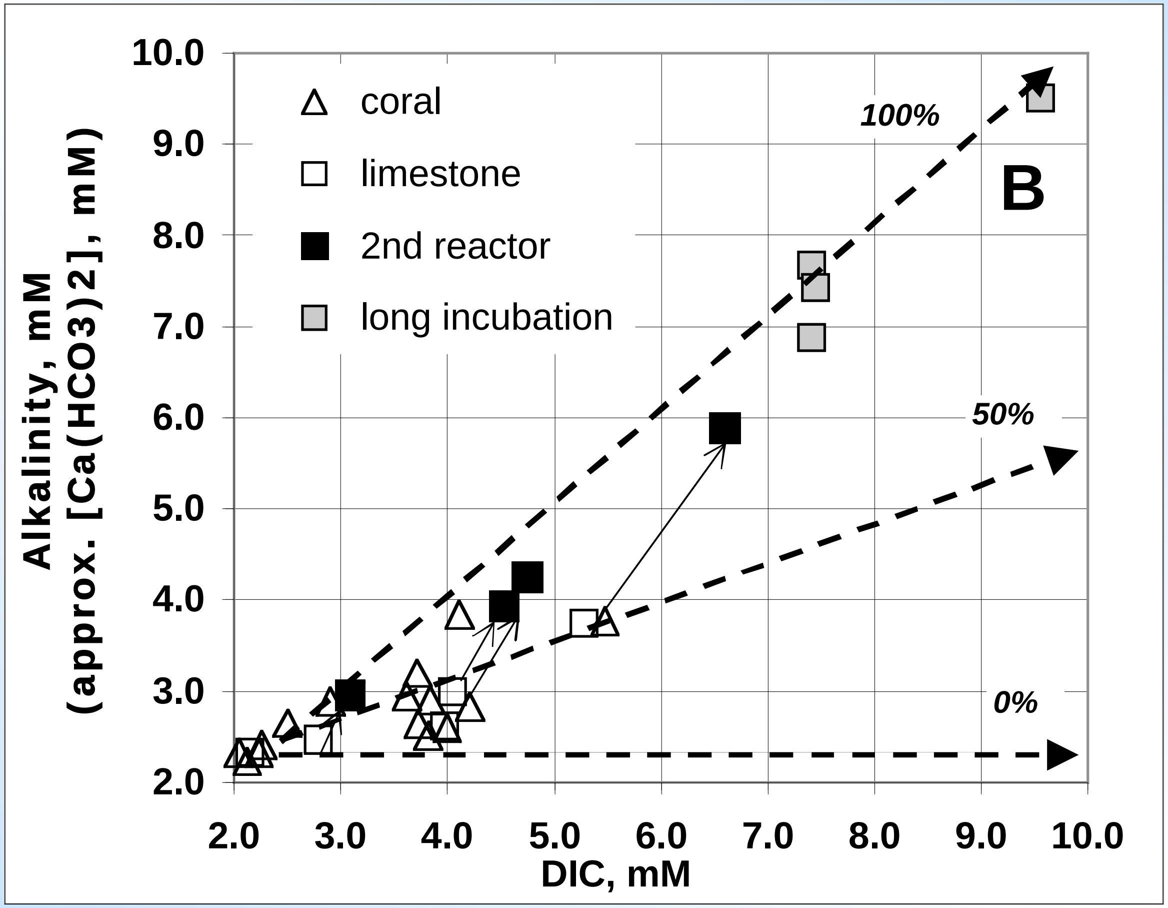


CO_2 Conversion to Calcium Bicarbonate: Single Reactor



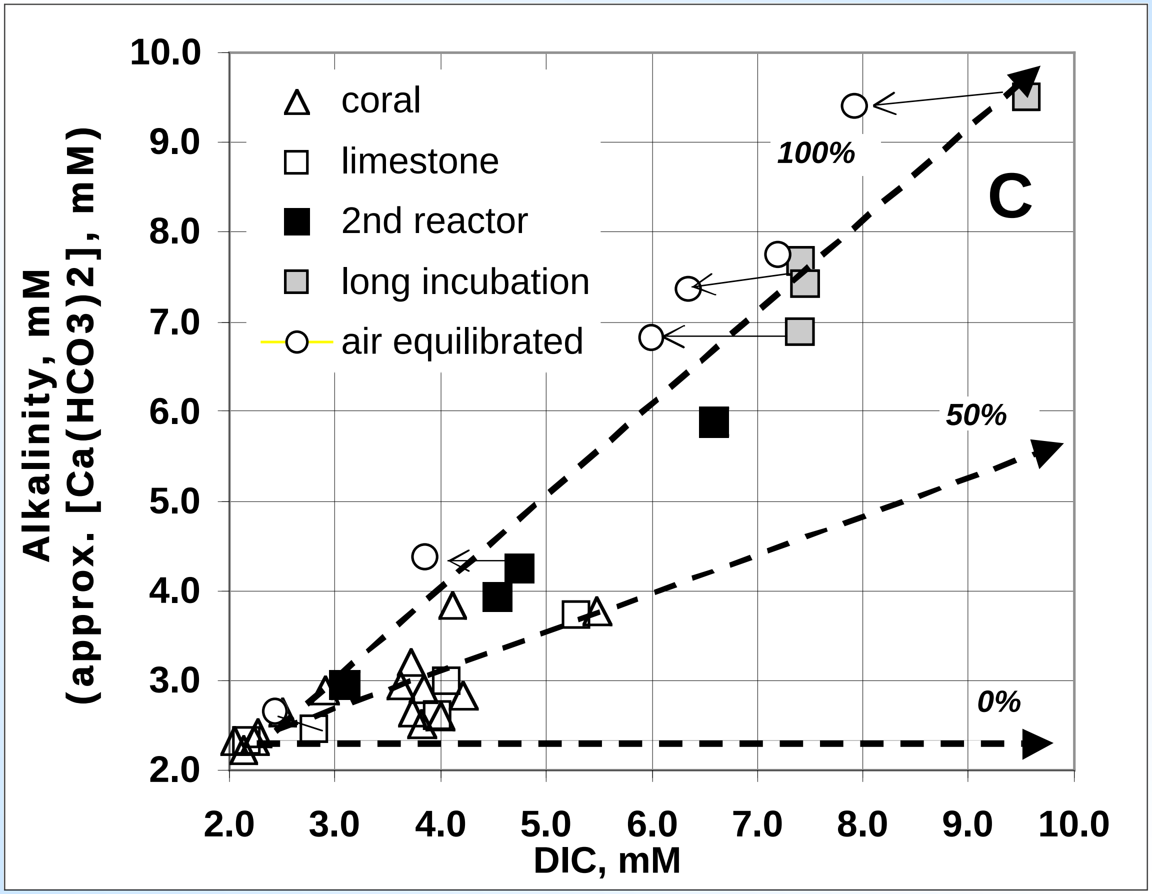
Conclusion: Single reactor effective in CO_2--> HCO_3^- conversion, but not very effective in CO_2--> $Ca(HCO_3)_2$ conversion

CO_2 Conversion to Calcium Bicarbonate: Second Reactor or Long Incubation



Conclusion: Greater exposure to carbonate = greater CO_2--> $Ca(HCO_3)_2$ conversion

CO_2 Conversion to Calcium Bicarbonate: Permanence?



Conclusion: 1) Little reversal of CO_2--> $Ca(HCO_3)_2$ even with full air equilibration
2) No chemical precipitation of carbonate

Effluent Effects on Downstream Biota - *Obelia* sp.

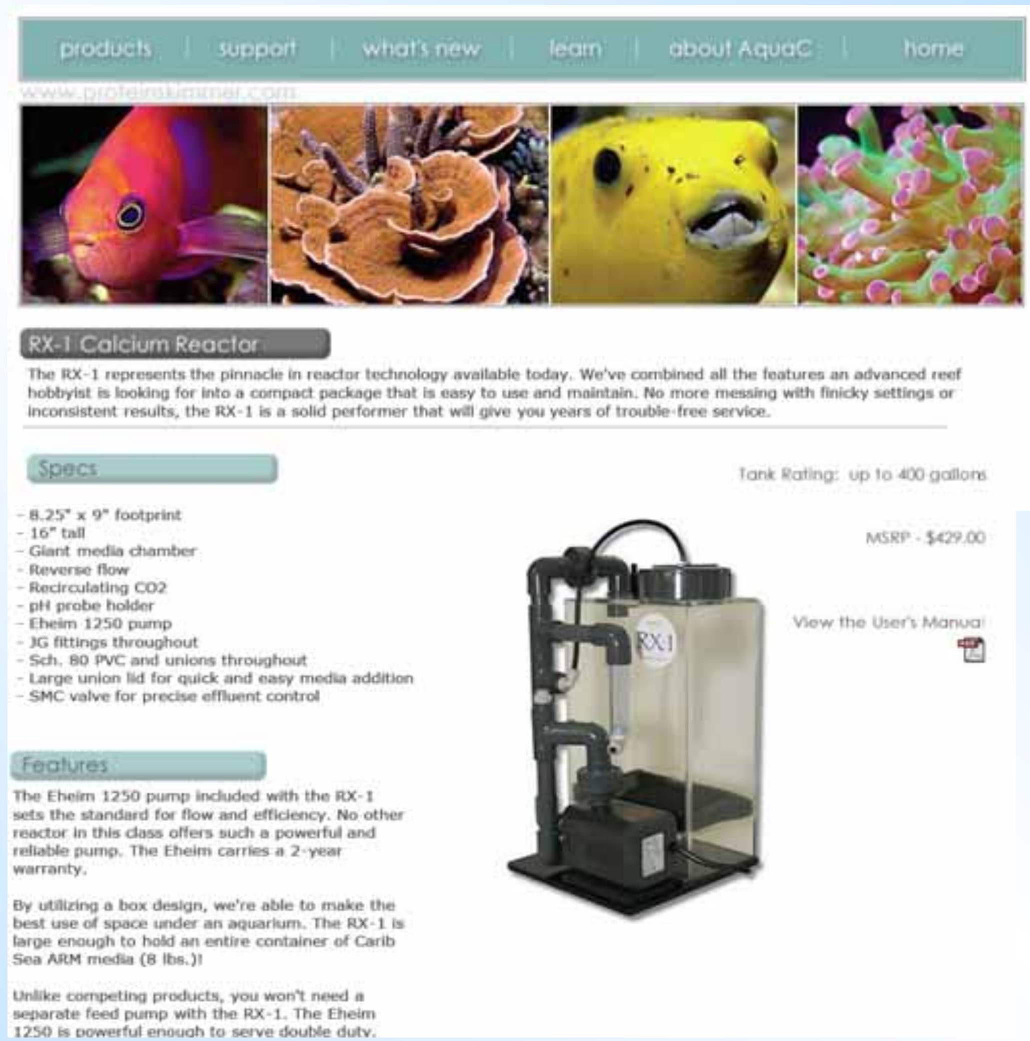
Added Alkalinity Source:		# Hydranths, Percent change	# Buds, Percent change	# Gonangia (initial = 0)	# Total polyps, Percent change
None	Mean=	98.9	168.2	0.0	121.5
	S.D.=	135.0	78.2	0.0	112.5
Coral	Mean=	101.4	275.0*	0.8	144.2
	S.D.=	58.3	67.3	0.5	55.5
Limestone	Mean=	144.1	182.9	4.0	212.6
	S.D.=	99.1	33.2	4.3	62.3

* statistically significant

Conclusion: Neutral to positive effects evident for *Obelia* sp.

Safety of AWL effluent?

In-home tank CO_2 + carbonate reactors routinely used to add alkalinity to saltwater aquariums!



Implications of study

- **Could limestone + seawater scrubbing of coastal CO_2 point sources, e.g., Calif. coastal power plants, be used to safely capture and sequester CO_2?**

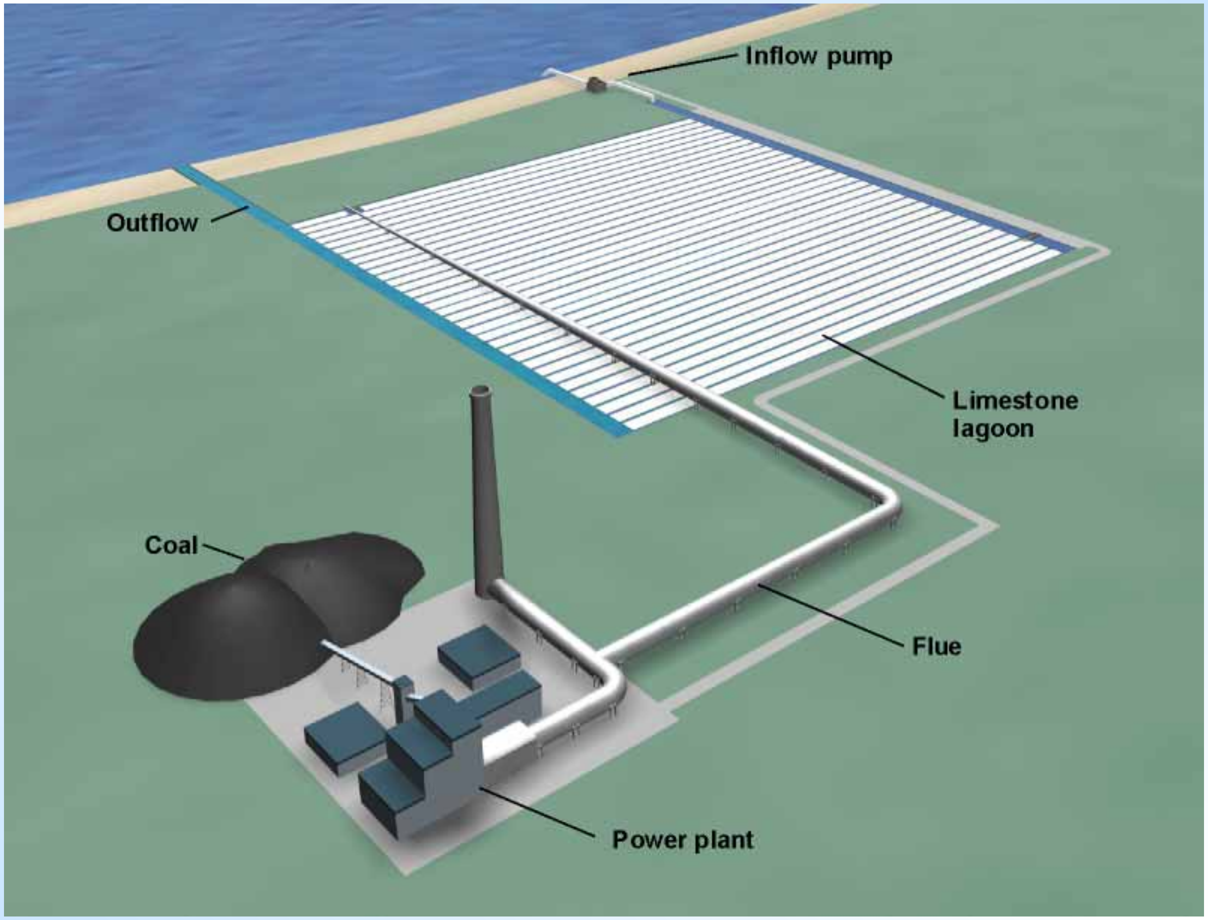
- **Remaining questions:**
  1) How much CO_2 mitigation?

  2) At what cost?

  3) How safe and with what environmental impact?

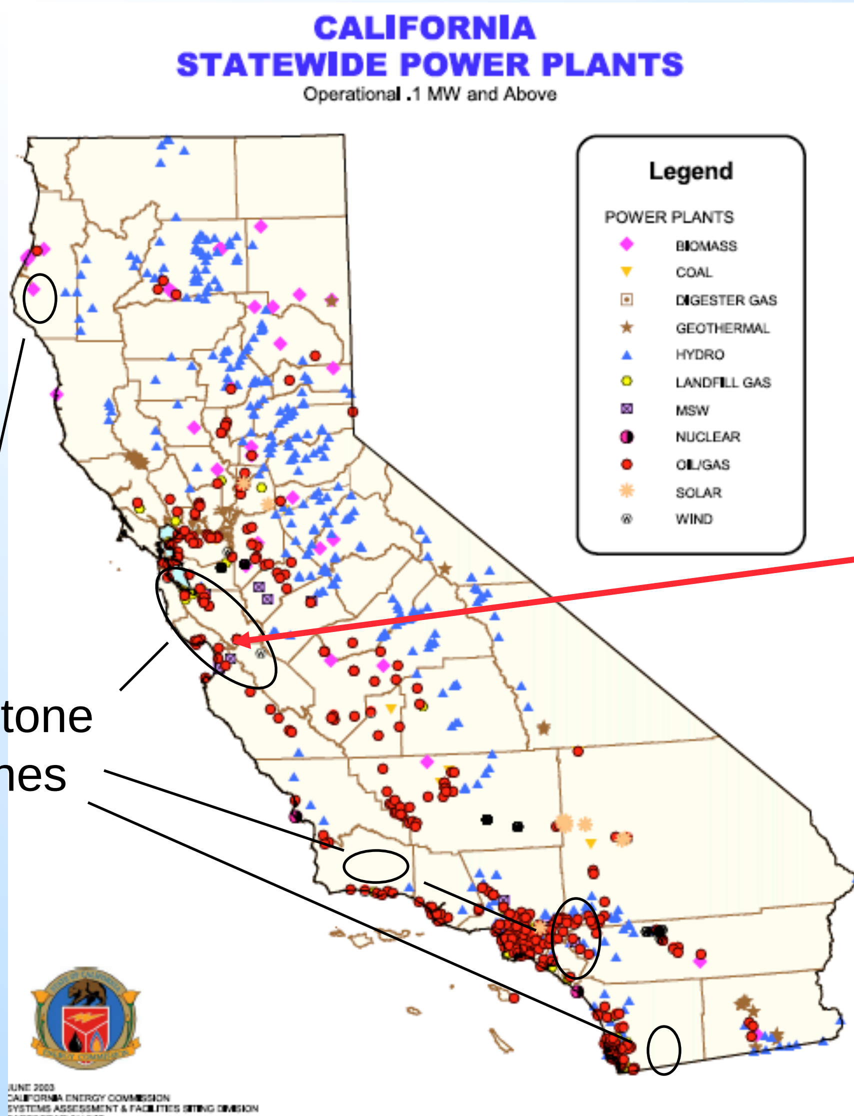
  4) Optimum reactor designs?

McDermott's limestone CO_2 scrubber concept



William Downs and Hamid Sarv. 2002. CO_2 CAPTURE AND SEQUESTRATION BY A LIMESTONE LAGOON SCRUBBER. McDermott Technology, Inc., Alliance, OH. 2nd Ohio CO_2 Reduction, Capture & Sequestration Forum, Ohio University, April 26 2002

Limestone availability vs. CA coastal power plant locations



Major Limestone Deposits/Mines

E.g., Moss Landing 2.5 GW power plant complex - largest single CO_2 emitted in state?

On site seawater availability

- 18 California coastal power plants already pump approx 1.4×10^{10} tonnes of seawater water per year for cooling.
- Assuming that 1 tonne of CO_2 can be absorbed and converted in 5,000 tonnes of seawater (extrapolated from lab obs), then about 2.8 million tonnes of CO_2/yr could be mitigated = 23% of annual coastal power plant emissions mitigated with “free” seawater.
- More CO_2 mitigation could be had with with additional seawater pumping, at added cost.

AWL Economics

- Estimated cost per tonne CO_2 sequestered, assuming coastal location:
  - Limestone -
    - 2.3 tonnes @ $4/tonne = $ 9.20
    - crushing from 10 cm to 1cm = $ 1.45
    - transport 100 km by rail = $ 8.00
  - Water -
    - 10^4 m^3, pumped 2 vertical meters = $ 7.57
  - Capital and maintenance = $ 2.50

TOTAL: **$ 29/tonne CO_2**

Compared to >$80/tonne for amine capture + geologic storage of CO_2 (CCS) from a conventional power plant (MIT, 2009)

Optimum AWL economics

Estimated cost per tonne CO_2 sequestered, assuming coastal location:

- Limestone -
  - 2.3 tonnes @ \$4/tonne = ~~\$ 9.20~~ *use free, nearby waste limestone*
  - crushing from 10 cm to 1cm = ~~\$ 1.45~~
  - transport 100 km by rail = ~~\$ 8.00~~
  - Water -
  - 10^4 m^3, pumped 2 vertical meters = ~~\$ 7.57~~ *use cooling water*
- Capital and maintenance = \$ 2.50

~~\$ 29/tonne CO_2~~

TOTAL: **<\$3/tonne CO_2**

Advantages of AWL:

- Abundant and cheap reactants:
  - Limestone - carbonates = $6x10^7$Gt C, fossil fuels = $4x10^3$Gt C; H_20 - ocean = $1.4x10^{18}m^3$
- Relatively innocuous waste products:
  - Primarily Ca^{2+}+ and HCO_3^- in solution; Avoids risk inherent with molecular CO_2; benefits to marine biota
- Not energy- or technology-intensive:
  - Does not require separate, costly CO_2 capture/concentration
  - Modify existing (seawater) FGD scrubbing technology
- Retrofittable to existing plants, and applicable to developing countries
- Relatively inexpensive
  - 10-20% US power plant emissions mitigated at <$30/ tonne CO_2

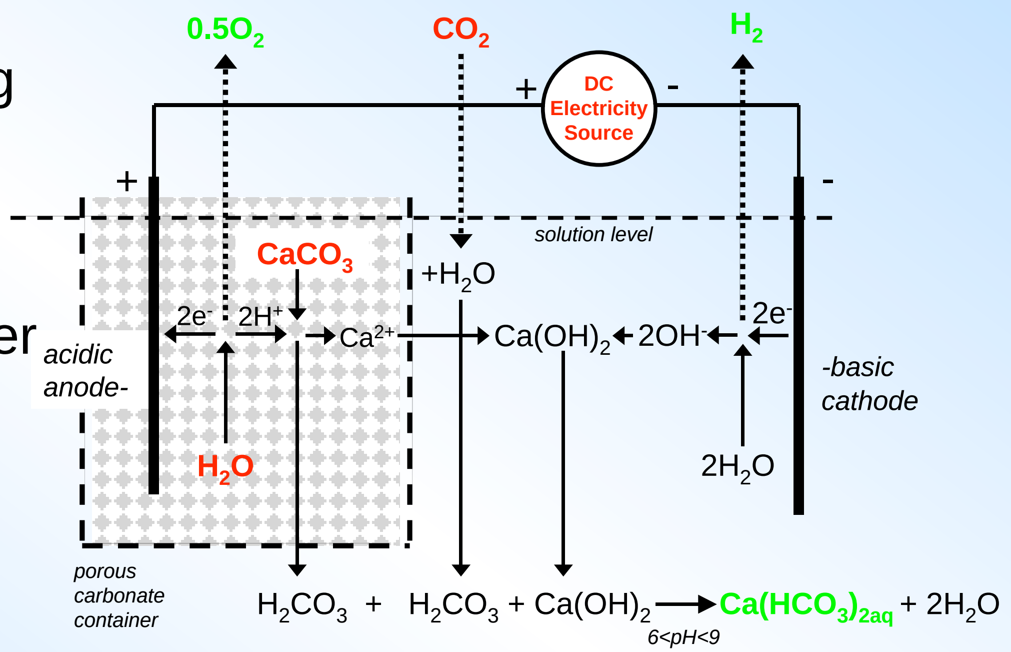
Impacts & Issues Needing Further Research:

- Local availability of limestone and water limits application
  - could be offset by piping CO_2 to favorable AWL sites
  - use inland saline aquifer or oil/water reservoirs?
- Marine biological impacts -
  - net beneficial?
  - trace contaminants from flue gas or limestone?
- Environmental, transportation, and economic impacts due to increased limestone mining/transport.
- What are optimum reactor designs and regional, national, and global markets? - R&D needed

Air CO_2 capture with "Juiced" AWL (JAWL)

Add renewable DC electricity to AWL chemistry to allow:

- Production of air CO_2 absorbing solutions while generating "super green" hydrogen
  - 22 tonnes CO_2 absorbed per tonne H_2 produced
  - thus, novel production of <u>carbon-negative hydrogen</u>
- Addition of alkalinity to seawater neutralizes or offsets ocean acidity



$CaCO_3$ as well as H_2O split
Net reaction: $CaCO_3 + H_2O + CO_2$ + DC ---> $0.5O_2 + H_2 + Ca(HCO_3)_{2aq}$
Net gain of $Ca(OH)_2$ leads to net gain of CO_2 at pH 6-9

Summary:

- Simple seawater+limestone scrubbing shown to be effective in removing up to 97% of point source CO_2.

- No negative downstream environmental effects observed (so far).

- In many coastal locations AWL would appear to be significantly less expensive than CCS.

- Using an electrified version of AWL, air capture of CO_2 has been demonstrated.

- All of the preceding need to be evaluated with larger scale R&D. Partners and funding sought.